The Crystal and Molecular Structure of Centrosymmetric Tetramethyl Quadruple-Layered Cyclophane*

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The title compound, $C_{40}H_{44}$, is monoclinic with $a = 24\cdot399$, $b = 8\cdot924$, $c = 13\cdot672$ Å, $\beta = 95\cdot53°$, space group $C2/c$, and $Z = 4$. The structure has been solved by interpreting the Patterson function and refined by the block-diagonal least-squares method to $R = 0\cdot084$ for 1567 reflexions. The molecule consists of two boat-shaped outer benzenes and two twist-shaped inner ones, a novel type of distorted benzene ring. The four benzene rings are stacked with a slight rotation between the outer and inner ones and with a parallel shift between the two inner ones.

Introduction

Layered cyclophanes in which more than two aromatic rings are constrained face-to-face with methylene bridges have been extensively investigated as models of transannular π-electron interaction since the study of Cram and his co-workers, and some anomalous behaviour in these highly strained molecules has been reported (Cram & Cram, 1971; Misumi, 1976; Horita, Kannen, Otsubo & Misumi, 1974). Crystal structure analysis has shown that such behaviour results from

transannular π-electron interaction and molecular strain due to close stacking of the benzene rings. Boat-shape deformation of benzene rings has been reported in the crystal studies of many double-layered cyclophanes (Brown, 1953; Lonsdale, Milledge & Rao, 1960; Hanson, 1962, 1971; Gantzel & Trueblood, 1965; Hope, Bernstein & Trueblood, 1972; Aono, Sakabe, Sakabe, Katayama & Tanaka, 1975).

The title compound (I) was synthesized by the scheme illustrated in Fig. 1. In this paper, the crystal structure of the title compound is reported to confirm the molecular configuration with point-group symmetry C_{2h} presumed from spectral and synthetic methods (Otsubo, Mizogami, Sakata & Misumi, 1971*a*, *b*, 1973;

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* Layered Compounds XXXII. Part XXXI: Horita, Sakata & Misumi (1976).
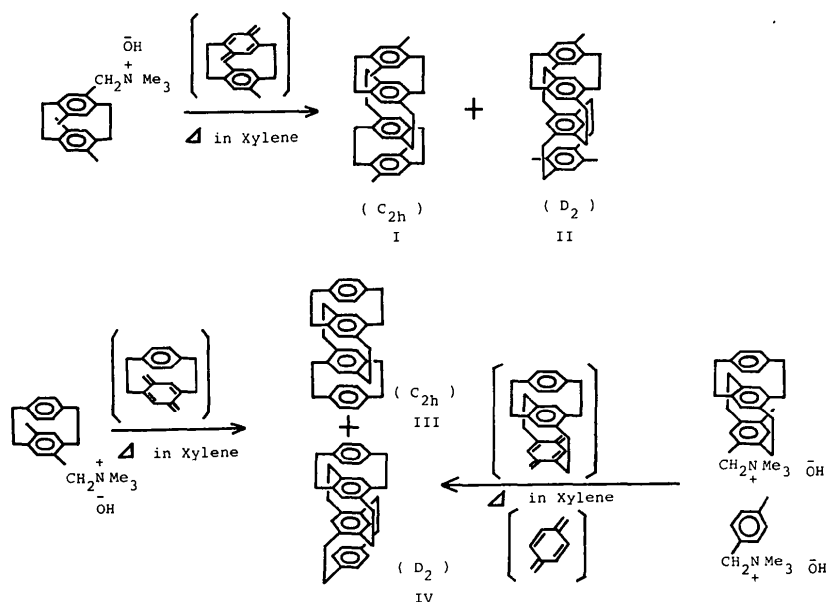

Fig. 1. Synthesis scheme of quadruple-layered cyclophanes I–IV.

Otsubo, Mizogami, Otsubo, Tozuka, Sakagami, Sakata & Misumi, 1973). The structure obtained shows boat-shaped outer benzenes and twist-shaped, a new type of deformation, inner benzenes (Mizuno, Nishiguchi, Otsubo, Misumi & Morimoto, 1972).

Experimental

The title compound was prepared by Otsubo and crystallized from toluene as colourless plates, elongated slightly along the **b** direction. The crystal has a perfect cleavage plane parallel to the b axis (Fig. 7).

Crystal data

$C_{40}H_{44}$, $M_r = 524 \cdot 8$, monoclinic, $a = 24 \cdot 399$, $b = 8 \cdot 924$, $c = 13 \cdot 672$ Å, $\beta = 95 \cdot 53°$, $V = 2693 \cdot 1$ Å^3, $D_m = 1 \cdot 18$, $D_c = 1 \cdot 176$ g cm^{-3}, $Z = 4$.

The space group was determined as Cc or $C2/c$ from oscillation and Weissenberg photographs. The latter space group was assumed from the statistical analysis of three-dimensional intensities. The density was measured by flotation in an aqueous zinc bromide solution at room temperature. Three-dimensional intensity data were collected on a Rigaku automatic four-circle single-crystal diffractometer with Zr-filtered Mo $K\alpha$ radiation. The crystal selected for data collection was a plate approximately $0 \cdot 20 \times 0 \cdot 10 \times 0 \cdot 30$ mm, mounted so that the b axis was coincident with the φ axis of the goniostat. The integrated intensities were measured with the $\theta-2\theta$ scan technique (scan speed $1°$ min^{-1}) in the range $[2\theta(\alpha_1) - 0 \cdot 60°]$ to $[2\theta(\alpha_1) + 0 \cdot 60°]$.

Background intensities were measured for 10 s at each end of a scan. During the data collection two standard reflexions (24,0,0 and 044) were periodically monitored to examine the stability of the electronics and the crystal. A total of 1741 independent reflexions were measured out to $\sin \theta/\lambda = 0 \cdot 55$, of which 174 were classed as unobserved. The intensities were corrected for Lorentz and polarization effects, but not for absorption.

Table 2. *Bond distances (Å) and their estimated standard deviations*

C(3)—C(4)	1·397 (7)	C(11)—C(12)	1·392 (7)
C(3)—C(8)	1·378 (7)	C(11)—C(16)	1·390 (7)
C(4)—C(5)	1·386 (7)	C(12)—C(13)	1·382 (7)
C(5)—C(6)	1·391 (7)	C(13)—C(14)	1·380 (7)
C(6)—C(7)	1·400 (7)	C(14)—C(15)	1·390 (7)
C(7)—C(8)	1·385 (7)	C(15)—C(16)	1·392 (7)
C(1)—C(14)	1·525 (7)	C(1)—C(2)	1·581 (8)
C(2)—C(3)	1·515 (7)	C(9)—C(10)	1·597 (9)
C(4)—C(19)	1·511 (8)	C(18)—C(17′)	1·550 (8)
C(6)—C(9)	1·504 (8)		
C(7)—C(20)	1·510 (9)		
C(10)—C(11)	1·521 (8)		
C(1)—H(1A)	1·06 (5)	C(1)—H(1B)	1·08 (5)
C(2)—H(2A)	1·05 (5)	C(2)—H(2B)	0·99 (4)
C(5)—H(5)	1·01 (4)	C(8)—H(8)	1·00 (4)
C(9)—H(9A)	0·99 (4)	C(9)—H(9B)	1·21 (5)
C(10)—H(10A)	1·07 (6)	C(10)—H(10B)	1·06 (6)
C(13)—H(13)	1·01 (4)	C(16)—H(16)	1·06 (4)
C(17)—H(17A)	1·11 (6)	C(17)—H(17B)	0·96 (6)
C(18)—H(18A)	1·03 (5)	C(18)—H(18B)	1·07 (5)
C(19)—H(19A)	0·93 (6)	C(19)—H(19B)	1·13 (6)
C(19)—H(19C)	0·97 (6)	C(20)—H(20A)	0·82 (6)
C(20)—H(20B)	1·10 (6)	C(20)—H(20C)	1·05 (6)

Table 1. *Atomic fractional coordinates and anisotropic thermal parameters ($\times 10^4$) of the carbon atoms*

Anisotropic thermal parameters are expressed in the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. The estimated standard deviations, given in parentheses, refer to the last significant figure.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	1633 (2)	5461 (6)	3927 (4)	27 (1)	153 (9)	102 (4)	−19 (5)	15 (4)	30 (10)
C(2)	985 (2)	5576 (6)	3904 (4)	26 (1)	150 (9)	110 (5)	17 (5)	5 (4)	9 (11)
C(3)	714 (2)	4071 (5)	4038 (4)	14 (1)	133 (8)	92 (4)	17 (4)	−3 (3)	5 (9)
C(4)	694 (2)	2961 (6)	3315 (3)	13 (1)	190 (9)	78 (4)	5 (5)	−2 (3)	4 (9)
C(5)	675 (2)	1483 (6)	3621 (4)	12 (1)	172 (8)	84 (4)	−5 (4)	−5 (3)	−75 (9)
C(6)	662 (2)	1083 (5)	4602 (4)	14 (1)	139 (8)	89 (4)	−20 (4)	−3 (3)	−5 (9)
C(7)	546 (2)	2204 (6)	5268 (3)	13 (1)	203 (9)	74 (4)	−19 (5)	2 (3)	−5 (10)
C(8)	582 (2)	3676 (6)	4960 (4)	15 (1)	172 (8)	81 (4)	8 (5)	4 (3)	−54 (10)
C(9)	894 (2)	−417 (6)	4930 (4)	22 (1)	164 (9)	126 (5)	−33 (6)	−8 (4)	30 (12)
C(10)	1508 (2)	−283 (6)	5448 (5)	26 (1)	152 (9)	156 (6)	−5 (6)	−16 (4)	44 (13)
C(11)	1789 (2)	1135 (5)	5134 (4)	15 (1)	118 (7)	119 (5)	−3 (4)	−13 (3)	12 (10)
C(12)	1960 (2)	1336 (5)	4200 (4)	13 (1)	145 (8)	100 (4)	0 (4)	−4 (3)	−76 (10)
C(13)	1933 (2)	2780 (6)	3834 (4)	13 (1)	171 (8)	80 (3)	−6 (5)	6 (3)	−25 (9)
C(14)	1855 (2)	4016 (5)	4411 (3)	14 (1)	139 (7)	85 (4)	−9 (4)	12 (3)	−31 (9)
C(15)	1916 (2)	3808 (5)	5423 (4)	12 (1)	139 (8)	88 (4)	6 (4)	11 (3)	−37 (9)
C(16)	1824 (2)	2366 (6)	5760 (4)	13 (1)	166 (8)	91 (4)	6 (5)	2 (3)	8 (10)
C(17)	2220 (2)	94 (7)	3652 (5)	22 (1)	206 (10)	148 (6)	4 (6)	−16 (4)	−184 (14)
C(18)	2146 (2)	5006 (6)	6129 (4)	21 (1)	186 (9)	103 (4)	−1 (6)	17 (4)	−103 (11)
C(19)	761 (2)	3323 (7)	2253 (4)	31 (1)	305 (13)	72 (4)	2 (7)	−2 (4)	43 (12)
C(20)	457 (2)	1897 (8)	6328 (4)	26 (1)	338 (14)	86 (4)	−45 (7)	11 (4)	−21 (13)

Determination and refinement of the structure

A three-dimensional Patterson function was calculated, from which basis a plausible model of the molecule was derived, excluding the methylene and methyl groups. Fixing the centre of this model at a centre of symmetry of the unit cell, the Fourier map revealed the methylene bridges and the methyl groups at the positions expected. When the R index had fallen to 0·28 by successive Fourier syntheses, the structure was refined by the block-diagonal least-squares method with unit weight for all reflexions. After several cycles of least-squares refinement, R converged to 0·18, and the difference synthesis clearly showed the aromatic H atoms, whereas the aliphatic H atoms were poorly resolved. Therefore, the positions of the latter H atoms were estimated from geometrical considerations. In a further refinement including H atoms, five reflexions, 800, 002,

202, $\bar{2}$02, and $\bar{4}$02, were excluded since they probably suffered from extinction. The final R index was 0·084 for all the observed reflexions. The final atomic coordinates, thermal parameters, and the corresponding standard deviations are listed in Table 1.* The computations were carried out with the programs of *The Universal Crystallographic Computing System – Osaka* (1973) and *The Universal Crystallographic Computing System* (I) (1967). Computation was performed on an NEAC 2200-700 computer at this University. Atomic scattering factors were taken from Suzuki (1958).

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* A list of structure factors and hydrogen atom coordinates and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32031 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Bond angles* (°) *and their estimated standard deviations*

C(4)—C(3)—C(8)	118·1 (5)	C(12)—C(11)—C(16)	117·2 (5)
C(3)—C(4)—C(5)	117·4 (5)	C(11)—C(12)—C(13)	116·4 (5)
C(4)—C(5)—C(6)	122·7 (5)	C(12)—C(13)—C(14)	122·9 (5)
C(5)—C(6)—C(7)	117·9 (5)	C(13)—C(14)—C(15)	117·1 (4)
C(6)—C(7)—C(8)	117·2 (5)	C(14)—C(15)—C(16)	116·6 (4)
C(7)—C(8)—C(3)	123·3 (5)	C(15)—C(16)—C(11)	121·9 (5)
C(2)—C(3)—C(4)	122·0 (5)	C(10)—C(11)—C(12)	123·3 (5)
C(2)—C(3)—C(8)	118·8 (4)	C(10)—C(11)—C(16)	119·1 (5)
C(19)—C(4)—C(3)	121·9 (5)	C(17)—C(12)—C(11)	122·5 (5)
C(19)—C(4)—C(5)	120·3 (5)	C(17)—C(12)—C(13)	120·8 (5)
C(9)—C(6)—C(5)	118·2 (5)	C(1)—C(14)—C(13)	119·4 (4)
C(9)—C(6)—C(7)	122·4 (5)	C(1)—C(14)—C(15)	123·0 (4)
C(20)—C(7)—C(6)	123·5 (5)	C(18)—C(15)—C(14)	122·7 (4)
C(20)—C(7)—C(8)	118·9 (5)	C(18)—C(15)—C(16)	120·3 (4)
C(2)—C(1)—C(14)	112·1 (4)	C(1)—C(2)—C(3)	112·7 (4)
C(6)—C(9)—C(10)	112·0 (5)	C(9)—C(10)—C(11)	111·5 (5)
C(12)—C(17)—C(18')	113·9 (5)	C(15)—C(18)—C(17')	112·6 (5)
C(14)—C(1)—H(1A)	109 (3)	C(9)—C(10)—H(10A)	103 (3)
C(14)—C(1)—H(1B)	110 (3)	C(9)—C(10)—H(10B)	107 (3)
C(2)—C(1)—H(1A)	112 (3)	C(11)—C(10)—H(10A)	110 (3)
C(2)—C(1)—H(1B)	113 (3)	C(11)—C(10)—H(10B)	108 (3)
C(1)—C(2)—H(2A)	109 (3)	C(12)—C(17)—H(17A)	111 (3)
C(1)—C(2)—H(2B)	102 (3)	C(12)—C(17)—H(17B)	110 (3)
C(3)—C(2)—H(2A)	111 (3)	C(18')—C(17)—H(17A)	107 (3)
C(3)—C(2)—H(2B)	107 (3)	C(18')—C(17)—H(17B)	114 (3)
C(6)—C(9)—H(9A)	108 (3)	C(15)—C(18)—H(18A)	108 (3)
C(6)—C(9)—H(9B)	104 (2)	C(15)—C(18)—H(18B)	114 (3)
C(10)—C(9)—H(9A)	108 (3)	C(17')—C(18)—H(18A)	105 (3)
C(10)—C(9)—H(9B)	104 (2)	C(17')—C(18)—H(18B)	101 (3)
C(4)—C(5)—H(5)	124 (2)	C(4)—C(19)—H(19A)	107 (4)
C(6)—C(5)—H(5)	112 (2)	C(4)—C(19)—H(19B)	121 (3)
C(3)—C(8)—H(8)	119 (2)	C(4)—C(19)—H(19C)	117 (3)
C(7)—C(8)—H(8)	116 (2)	C(7)—C(20)—H(20A)	98 (4)
C(12)—C(13)—H(13)	120 (2)	C(7)—C(20)—H(20B)	114 (3)
C(14)—C(13)—H(13)	117 (2)	C(7)—C(20)—H(20C)	114 (3)
C(11)—C(16)—H(16)	120 (2)		
C(15)—C(16)—H(16)	118 (2)		
H(1A)—C(1)—H(1B)	100 (4)	H(2A)—C(2)—H(2B)	114 (4)
H(9A)—C(9)—H(9B)	121 (3)	H(10A)—C(10)—H(10B)	117 (4)
H(17A)—C(17)—H(17B)	99 (5)	H(18A)—C(18)—H(18B)	116 (4)
C(19A)—C(19)—H(19B)	88 (5)	H(19A)—C(19)—H(19C)	121 (5)
C(19B)—C(19)—H(19C)	100 (4)	H(20A)—C(20)—H(20B)	112 (5)
C(20A)—C(20)—H(20C)	109 (5)	H(20B)—C(20)—H(20C)	109 (5)

Results and discussion

The molecular geometry is illustrated in Fig. 2. Bond lengths and angles are summarized in Tables 2 and 3 respectively. The thermal ellipsoids are shown in Fig. 3. The most remarkable feature is the distortion of the
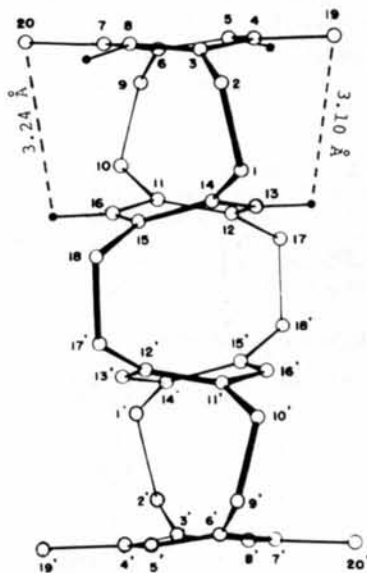

Fig. 2. The molecular structure viewed along **b**.

benzene rings from regular hexagons with marked deviations of the substituents. Thus, the outer benzene rings are boat-shaped as in the case of many other cyclophanes. The bending angles, α and β, are shown in Table 4 together with those of two paracyclophanes. The values of the present molecule are comparable to those of [2.2]paracyclophane. On the other hand, the inner benzene rings are twisted by two upper and two lower methylene bridges. The dihedral angle between the planes through C(12), C(13) and C(14), and C(11), C(16) and C(15) [or C(12'), C(13') and C(14'), and C(11'), C(16') and C(15')] is 13·4° as shown in Fig. 4. This distortion is more severe than the former, i.e. the atomic displacements (−0·16 − 0·14 Å) from the least-squares plane through the six atoms of the inner benzene ring are considerably larger than those of the outer ring (−0·11 − 0·08 Å) (Fig. 5). Intramolecular atomic short contacts between the benzene rings are shown together with those of [2.2]paracyclophane in Table 5. Such intriguing deformation of the benzene rings in the present molecule is undoubtedly attributed to the π-electron repulsion taking place both upward and downward of the sandwiched inner benzenes.

Of the bond lengths of the present molecule, the C(1)–C(2) and C(9)–C(10) bonds are longer by 0·02–0·03 Å than those in [2.2]paracyclophane (1·562 Å), indicating more severe repulsion. On the other hand, the corresponding bond [C(17)–C(18') or C(18)–C(17')] between the two inner benzene rings is shorter than that in [2.2]paracyclophane. This may be
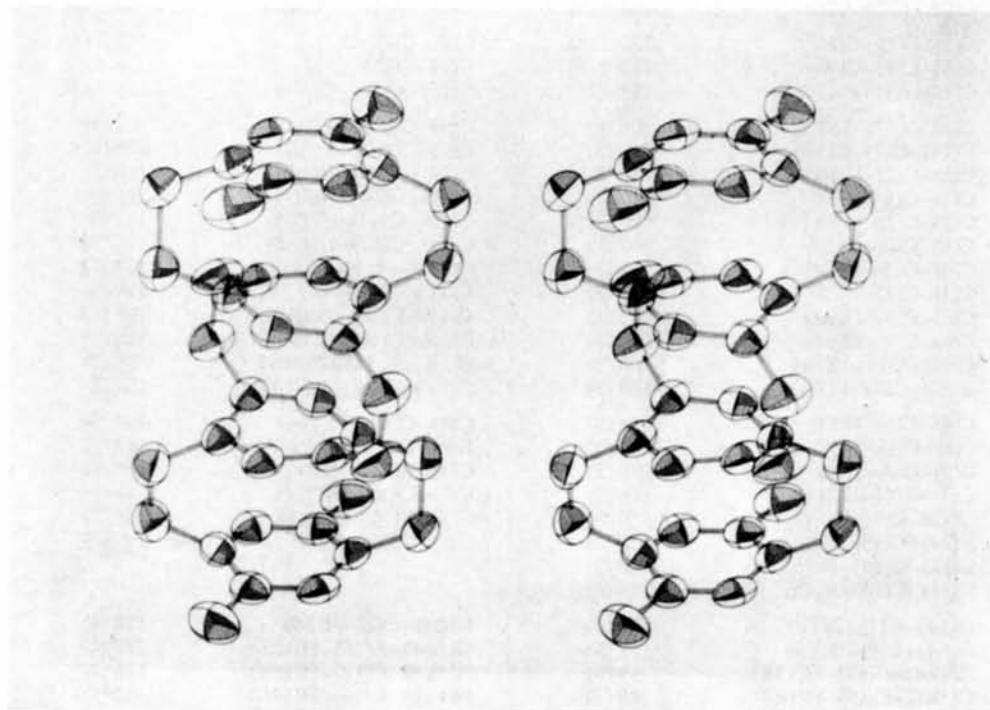

Fig. 3. A stereo pair showing the molecular structure; the thermal ellipsoids are of 50% probability.

caused by reduction of the repulsive force as a result of the twist deformation of the two inner benzene rings. The average C—C bond lengths of outer and inner benzene rings are 1·390 and 1·388 Å, respectively, not significantly different from those of benzene (1·392–1·397 Å).

The molecular strain markedly affects the bond angles. As shown in Table 3, the bond angles at the C
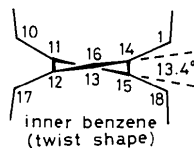

Fig. 4. Out-of-plane distortion of inner benzene rings.

Table 4. *Bending angles* (°) *of boat-shaped benzene rings*

* α_1 and α_2 are the dihedral angles between the mean planes of C(4)—C(5)—C(7)—C(8) and C(4)—C(3)—C(8), and of C(4)—C(5)—C(7)—C(8) and C(6)—C(5)—C(7). β_1 and β_2 are the angles between the interatomic vector of C(2)—C(3) and the mean plane of C(4)—C(3)—C(8), and between C(9)—C(6) and C(6)—C(5)—C(7).
† Hope, Bernstein & Trueblood (1972).
‡ Coulter & Trueblood (1963).

Table 5. *Intramolecular atomic short contacts* (Å) *between benzene rings*

Present molecule		
Outer–inner	Inner–inner	
2·78 [C(3)—C(14)]	3·31 [C(11)—C(14')]	2·78 [C(13)—C(14)]
3·04 [C(4)—C(13)]	2·74 [C(12)—C(15')]	3·09 [C(4)—C(13)]
3·16 [C(5)—C(12)]	3·03 [C(13)—C(16')]	
2·78 [C(6)—C(11)]		
3·13 [C(7)—C(16)]		
3·26 [C(8)—C(15)]		
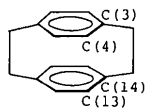
atoms to which the substituents are attached are smaller than the normal value, whereas the others are slightly larger. This is explained by double book-like bending of the benzene ring (Wynberg, Nieuwport & Jonkman, 1973) to reduce π-electron repulsion and steric compression of the substituents.

Aromatic H atoms have been located with an accuracy of 0·04 Å, and the average C—H distance is 1·02 Å (Table 3). The H atoms, H(5) and H(8), of the outer benzene ring are slightly displaced from the mean planes through C(4), C(5) and C(6), and C(3), C(8) and C(7), respectively, toward the centre of the molecule in the same manner as in many cyclophanes (Fig. 2). The H atoms H(13) and H(16) of the inner benzene ring are on the mean plane of the six C atoms, C(11) to C(16), within experimental error. On the other hand, unexpected displacement of the methyl groups C(19) and C(20) is interpreted by the additional repulsion between the methyl groups and the inner aromatic H atoms, C(19)···H(13) and C(20)···H(16) respectively (Fig. 2). This repulsion reflects the downfield shift (steric compression effect, σ_{CE}) of the inner aromatic protons H(13) and H(16) by 0·38 p.p.m. compared to the corresponding protons of compound III in ¹H-NMR spectra (Otsubo, Mizogami, Sakata & Misumi, 1973).
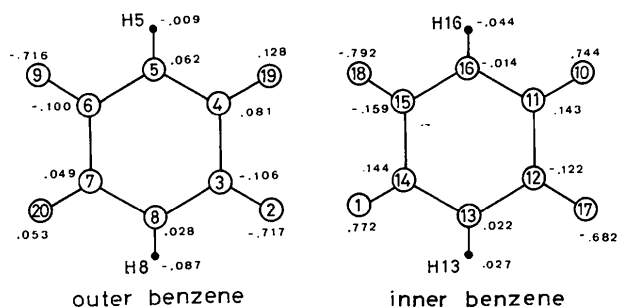

Fig. 5. The deviations from the mean plane defined by the six carbon atoms of the benzene ring.
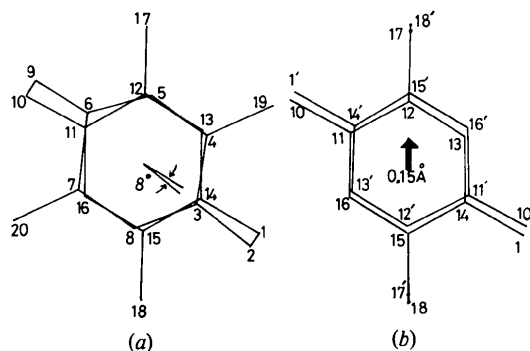

Fig. 6. Stacking modes of the benzene rings in the molecule. (a) The outer ring relative to the inner ring and (b) the inner rings relative to each other.

Fig. 6 shows the stacking mode of the four benzene rings. The outer and the inner rings are stacked with a slight rotation of 8°, and the two inner rings reveal a mutual parallel displacement of 0·15 Å. Compared with the rotational vibration of the benzene rings in crystalline [2.2]paracyclophane (Hope, Bernstein & Trueblood, 1972), the rotation of the present molecule is restricted to one side owing to the repulsions between two methylene groups [C(1)···C(18) and C(10)···C(17)]. The displacement most likely occurred in order to minimize the repulsions of the π-electron cloud and between substituents, i.e. proton eclipsing in the methylene bridges, methyl–methylene repulsion, and methylene–methylene repulsion.

The molecular packing in the crystal is illustrated in Fig. 7. The (200) plane shows that the crystal has a perfect cleavage plane. The intermolecular contacts appear to be normal; the shortest, 3·58 Å, is between C(4) of the molecule at (x,y,z) and C(19) of that at $(-x, y, \frac{1}{2} - z)$.
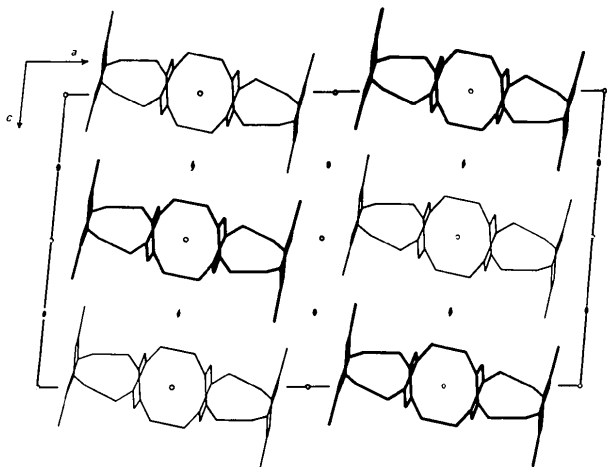

Fig. 7. The crystal structure viewed along **b**.

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